

1772-283



Jc929 U.S. PTO  
09/768733  
01/24/01

# Kongeriget Danmark

Patent application No.: PA 2000 00118  
Date of filing: 25 January 2000  
Applicant: Haldor Topsøe A/S  
Nymøllevej 55  
DK-2800 Kgs. Lyngby

This is to certify the correctness of the following information:

The attached photocopy is a true copy of the following document:

- The specification, claims and abstract as filed with the application on the filing date indicated above.



Patent- og  
Varemærkestyrelsen  
Erhvervsministeriet

Taastrup 22 December 2000

Karin Schlichting  
Head Clerk



# **HALDOR TOPSØE A/S**

NYMØLLEVEJ 55 · P.O. BOX 213 · DK-2800 LYNGBY · DENMARK · VAT. NO. DK 41853816  
TELEPHONE: +45 4527 2000 · FAX: +45 4527 2999 · WWW.HALDORTOPSOE.COM · REG.NO. 52370

25 January 2000

DK3037237003

HABS/AKN

Modtaget

25 JAN. 2000

PVS

## **Process for Reduction of Content of Sulphur Compounds and Polyaromatic Hydrocarbons in Distillate Fuels**

The present invention is directed towards the improvement of distillate fuels. More particularly, the invention relates a process for reducing concentration of sulphur and polyaromatic compounds in those fuels.

5

Many countries are in the process of tightening specifications for the sulphur content of diesel fuels. For example, current legislation specifies a maximum sulphur content in diesel in the European Union of 50 wppm from the year 2005, and in California 15 wppm from 2004. Current specifications for low sulphur diesel fuel in many cases also include limits for the maximum content of polyaromatic hydrocarbons, for the maximum density (or specific gravity) and for the minimum cetane number. It is expected that the specification for all three properties will be tightened further in the near future to meet requirements for reduced emissions from diesel engines.

#### DESCRIPTION OF PRIOR ART

20

Sulphur can be removed by means of hydrotreating. The diesel fuel is passed over a suitable catalyst under a pressure of hydrogen and at elevated temperatures. Typical conditions are hydrogen pressure = 15-70 bar; average reactor temperature 300-400°C; liquid hourly space velocity (LHSV) = 0.5-3.0 m<sup>3</sup>oil/m<sup>3</sup>catalyst/h. The exact conditions will depend on the type of feedstock, the required degree of desulphurisation and the desired run length. The reactor temperature on fresh catalyst (start of run) is normally at the lower end of the above range, and as the catalyst deactivates the reactor temperature is raised to compensate for loss of catalyst activity. The end of the run is normally

reached when the design temperature for the reactor is reached, which is decided by the metallurgy of the reactor. The lower the start of run temperature and the higher the end of run temperature, the longer the catalyst run length for a given rate of deactivation. For a refiner, the run length is a very important consideration. A shorter run length means high costs due to a higher rate of catalyst replacement, and relatively more downtime (i.e. time off-stream) for catalyst change-out with a resultant loss of revenue due to reduced diesel fuel production.

A hydrotreating unit is normally designed for a fixed LHSV ( $\text{m}^3\text{oil}/\text{m}^3\text{catalyst}/\text{h}$ ) based on a required throughput of feedstock and a fixed reactor (catalyst) volume. Lower sulphur product can be obtained by lowering LHSV (e.g. by adding extra catalyst volume). As an example, starting with a feedstock containing 1% sulphur it requires typically 3-4 times more catalyst volume to produce a diesel containing 50 wppm sulphur than to produce a diesel containing 500 wppm sulphur at the same reactor temperature and hydrogen pressure. Alternatively, the start of run temperature can be raised to obtain a lower product sulphur at unchanged LHSV. In the above example, the start of run temperature would typically need to be raised 35-45°C in order to reduce product sulphur from 500 wppm to 50 wppm. In the first instance, the addition reactor capacity represents a substantial investment, and in the second instance, the run length is reduced considerably. In many cases, units designed to meet the more stringent sulphur specifications will make use of both possibilities. For example, the catalyst volume could be increased by a factor 2-3 (LHSV reduced by a factor 2-3) and the start of run temperature in-

creased by 10-20°C. By doing so the same run length could be achieved, because the rate of deactivation is lower at the lower LHSV and this compensates for the smaller temperature span between start of run and end of run.

5

Further restrictions on run length may be imposed if the diesel specifications require a reduction in polyaromatic hydrocarbon content in addition to reduction in sulphur. Polyaromatic hydrocarbons (PAH) are defined as fused multi-  
10 ring aromatic compounds containing two or more aromatic rings. The concentration of PAH can be measured by the analysis method IP 391-95. PAH compounds react readily at hydrotreating conditions. Three-ring aromatic compounds are hydrogenated to two-ring aromatic compounds, which are hy-  
15 drogenated to monoaromatic hydrocarbons. The monoaromatic compounds react slowly at typical distillate hydrotreating conditions to form naphthenes. The reactions are reversible and at high reaction temperatures and low hydrogen pressure the conversion of the PAH compounds is thermodynamically  
20 limited by equilibrium. As a consequence, the conversion of PAH compounds in a hydrotreating unit producing low sulphur diesel might at first increase as reaction temperature is increased, and then decrease as temperature is increased further owing to equilibrium constraints at the higher tem-  
25 perature. This can have a negative influence on the run length as illustrated in the following example:

A hydrotreating unit is designed to produce a diesel containing 50 wppm at a start of run temperature of 350°C. The  
30 reactor is designed to operate up to an average catalyst temperature of 400°C. The run length (based on a 50°C temperature span) is two years. The PAH content of the feed is

10 wt% and at start of run the product produced contains 2 wt% PAH. Suppose that a new specification for diesel is imposed limiting the PAH content to 3 wt%. This is achievable at start of run but at the conditions employed in the unit, 5 the 3% limit is exceeded at temperatures above 365°C. This means that the temperature span from start of run to end of run is reduced to 15°C, reducing run length to about one third. This is clearly unacceptable and would necessitate considerable investment in extra reactor volume or construction of a new unit at higher hydrogen pressure in order to maintain run length. 10

The temperature at which the PAH equilibrium is met will depend on a number of factors including, hydrogen pressure, 15 feed PAH content and composition, LHSV and product requirement. Thus, increasing pressure or reducing LHSV can extend the run length, but both measures require costly investments.

20 It is thus the general object of the invention to provide a process for the production of a low sulphur distillate fuel having a low content of polyaromatic hydrocarbons and thereby improved density and cetane number properties.

25

#### SUMMARY OF THE INVENTION

The present invention is a process for achieving a low PAH content in distillate streams with only slight additional 30 investment in reactor volume and without reduction in run length. The essence of the inventive process consists of cooling the effluent exiting the hydrotreating reactor and passing the cooled product through a small post-treat reac-

tor containing a suitable catalyst. The PAH content of the product exiting the hydrotreating reactor is reduced in the post treatment reactor owing to the more favourable equilibrium conditions at the lower temperature. As a consequence, the end of run temperature in the main hydrotreating reactor is not limited by the PAH content of the product exiting the main reactor, and a lower overall reactor volume (main hydrotreater plus post treat reactor) is required for a given run length. In another embodiment of the process the final bed of the main hydrotreating reactor is operated at lower temperature instead of using a post-treatment reactor. The process can be used to lower the density and raise the cetane number of the diesel product. Since the densities of PAH compounds are in general higher than the corresponding monoaromatic compounds, lowering the PAH content of the product also lowers the density of the product. In the same way, the cetane number and cetane index of PAH compounds are lower than the corresponding monoaromatic compounds, and reducing PAH content results in an increase in cetane number and cetane index.

#### DETAILED DESCRIPTION OF THE INVENTION

The petroleum distillates used in the present invention boil in the range 120-450°C and have a PAH content in the range 5-50 wt%. Examples of distillates include straight run fractions from an atmospheric crude distillation, light fractions from a vacuum crude distillation, the distillate obtained by fractionation of the product from a fluid catalytic cracking unit, distillate obtained by fractionation of oils from thermal cracking processes including cooking, and mixtures thereof. The process is particularly suitable

for blends of distillate containing thermal cracked oils and fluid catalytic cracking distillate because these oil generally have a high PAH content.

5 The process layout is illustrated in Fig. 1. Feedstock is mixed with hydrogen, heated in the furnace (1) and passed through the hydrotreating reactor (2). The conditions used in the hydrotreating reactor are the same as those normally used for deep desulphurisation of distillates i.e. typical  
 10 hydrogen pressure = 15-70 bar; typical average reactor temperature = 300-400°C; typical LHSV = 0.5-3.0 m<sup>3</sup>oil/m<sup>3</sup>catalyst/h, and typical hydrogen gas to oil ratio = 100-1000Nm<sup>3</sup>/m<sup>3</sup>. The effluent from the hydrotreater is cooled to a suitable temperature by heat exchange with the  
 15 feed to the hydrotreater (3) or by other means before passing to the post-treatment reactor (4). The temperature employed in the post-treatment reactor will typically be in the range 250°C to 350°, and will typically be at least 50°C lower than the outlet temperature of the hydrotreater.  
 20 The LHSV in the post-treatment reactor will typically be in the range 2-20 m<sup>3</sup>oil/m<sup>3</sup>catalyst/h. and total pressure will be at the same level as that in the hydrotreating reactor.

The catalyst used in the hydrotreating reactor may be any  
 25 catalyst used for hydrotreating distillate streams and known in the art. The catalyst contains at least one metal on a porous refractory inorganic oxide support. Examples of metals having hydrotreating activity include metals from groups VI-B and VIII e.g. Co, Mo, Ni, W, Fe with mixtures  
 30 of Co-Mo, Ni-Mo and Ni-W preferred. The metals are employed as oxides or sulphides. Examples of porous material suitable as support include alumina, silica-alumina, alumina-



titania, natural and synthetic molecular sieves and mixtures hereof, with the alumina and silica-alumina being preferred.

- 5 The catalyst used in the post treatment reactor may be any catalyst used for hydrotreating distillate streams. Preferred catalysts are Ni-Mo, Co-Mo and Ni-W on alumina.

10 The active metal on the catalyst may be either presulphided or in-situ sulphided prior to use by conventional means.

15 The hydrotreating reactor section may consist of one or more reactors. Each reactor may have one or more catalyst beds. The function of the hydrotreating reactor is primarily to reduce product sulphur. Owing to the exothermic nature of the desulphurisation reaction, the outlet temperature is generally higher than the inlet temperature. Some reduction of PAH may be achieved in the hydrotreating reactor especially at start of run conditions. As the catalyst activity declines due to deactivation by carbonaceous deposits, sintering of the active phase and other mechanisms, the inlet temperature to the hydrotreating reactor is raised, resulting in an increased outlet temperature. This will result at some point in an increase in the PAH content in the effluent of the hydrotreater reactor due to equilibrium limitations. The temperature at which this occurs will depend on the amount and type of aromatic compounds in the oil, and the hydrogen partial pressure in the unit.

20

25

- 30 The function of the post-treatment reactor is primarily to reduce the PAH content. The lower temperature in the post-treatment reactor ensures more favourable conditions for

the thermodynamic equilibrium between PAH compounds and monoaromatic compounds. The reduction in PAH will result in a reduction in the product oil density and an increase in product oil cetane number, both of which are desirable.

- 5 Only slight reduction in the sulphur content will be achieved at the conditions in post-treatment reactor.

The present invention is illustrated in the following examples of specific embodiments:

10

**Example 1 (comparative)**

- Feedstock A (Table 1) was hydrotreated in a semi-adiabatic pilot plant unit running with an outlet temperature of
- 15 390°C - a temperature, which normally is considered as end of run (EOR) conditions. The pressure was 30 Bar. Pure hydrogen was used as gas. Feedstock A is a mixture of 50% cycle oil and 50% straight run gas oil (SRGO).

**Table 1**

Properties of feedstock used in the following examples:

Properties	Feedstock A	Feedstock B
SG 60/60	0.8899	0.8703
S (wt%)	0.931	1.462
N (wt ppm)	388	231
Aromatics (wt%)		
Mono-	16.2	17.2
Di-	22.8	15.1
Tri-	7.7	4.6
Distillation, D2887		
(°C)	185.1	194.3
5	210.2	215.3
10	254.0	258.3
30	286.6	291.8
50	318.4	324.6
70	366.8	369.3
90	390.1	387.5
95		

5

Product properties are shown in Table 2.

**Table 2**

Properties of product in Example 1:

Properties	Product A
SG 60/60	0.8727
S (wt ppm)	55
Aromatics (wt%)	
Mono-	28.6
Di-	15.3
Tri-	5.3

5

This product contains 20.6 wt% PAH, which would be typical for a product obtained at EOR conditions in a unit where the hydrogen partial inlet pressure is 30 bar (without taken into account the evaporated diesel), if the feedstock contains 50% cycle oil and 50% SRGO.

10

**Example 2**

Product A from example 1 is further hydrotreated at lower temperatures at different LHSV. The pressure is 30 Bar, which is identical to the pressure at which product A was obtained. When product A was obtained in the first hydro-treater, the gas phase had a certain amount of H<sub>2</sub>S, which is a function of the amount of sulphur in the feed, the gas to oil ratio and the degree of desulphurisation. Product A was doped with a sulphur component in order to simulate the amount of H<sub>2</sub>S that would be in the gas phase without inter-stage removal of H<sub>2</sub>S (and other gases), when product A and the gas in equilibrium herewith is produced in the first

15

20

hydrotreatment (Example 1). A Ni-Mo on alumina catalyst is used in this test. The results are shown in Table 3.

**Table 3**

5

Properties of products in Example 2:

Temperature (°C)	LHSV (h <sup>-1</sup> )	SG 60/60	Di- aromatics (wt%)	Tri- aromatics (wt%)	PAH (wt%)
270	2.0	0.8698	7.8	4.0	11.8
270	6.0	0.8718	12.1	4.6	16.7
300	4.0	0.8679	6.3	3.4	9.7
300	10.0	0.8710	9.2	3.7	12.9
330	2.0	0.8665	6.4	2.6	9.0
330	6.0	0.8683	8.0	3.5	11.5

10 There is virtually no further sulphur removal in this low-  
temperature hydrotreatment, but it is quite obvious that a  
large amount of the PAH can be removed at a relatively high  
LHSV. The process, in which poly-aromatics are removed at  
lower temperature, is possible both with and without inter-  
15 stage removal of H<sub>2</sub>S. It is clear from the above example  
that there is an optimum for removal of PAH around 300-  
330°C at 30 bar hydrogen partial pressure at the inlet  
(without taken into account the evaporated diesel).

20 **Example 3**

Product A from Example 1 is further hydrotreated at a  
higher pressure than in Example 2. At T=300°C, P=45 Bar in-  
let hydrogen partial pressure (without taken into account  
25 the evaporated diesel) and LHSV=2h<sup>-1</sup> the PAH are removed  
down to 2.9 wt% di-aromatics and 1.8 wt% tri-aromatics. The

specific gravity (SG 60/60) is 0.8638. It is clear that a higher hydrogen partial pressure increases the saturation of the poly-aromatic compounds. Product A was again doped with a sulphur component in order to simulate the amount of H<sub>2</sub>S that would be in the gas phase without inter-stage removal of H<sub>2</sub>S (and other gases), when product A and the gas in equilibrium herewith is produced in the first hydro-treatment (Example 1). A Ni-Mo on alumina catalyst is used in this test. There is virtually no further sulphur removal in this low-temperature hydrotreatment.

#### Example 4 (comparative)

Feedstock B (Table 1) was hydrotreated at two different conditions in an isothermal pilot plant unit at T=390°C - a temperature, which normally is considered as end of run (EOR) conditions. The pressure was 32 Bar. Pure hydrogen was used as gas. Hydrogen to oil ratio is 336 Nl/l. Feedstock B is a mixture of 50% light cycle oil (LCO) and 50% straight run gas oil (SRGO). A Co-Mo on alumina catalyst is used in this test. The properties of the products from the test are shown in Table 4.

Table 4

Properties of products in Example 4:

LHSV (h <sup>-1</sup> )	Sulphur (wt ppm)	Di- aromatics (wt%)	Tri- aromatics (wt%)	PAH (wt%)
1.8	55	8.6	2.9	11.5
0.9	10	8.7	2.9	11.6

The two products have the same amount of poly-aromatic compounds, although they are quite different in their residual sulphur content. The reason for this result is that all aromatic compounds due to the high reaction temperature are close to the equilibrium between tri-aromatic  $\leftrightarrow$  di-aromatic  $\leftrightarrow$  mono-aromatic  $\leftrightarrow$  naphthene, and therefore no effect of LHSV on the amount of PAH are observed.

#### Example 5

Product B from Example 4 is further hydrotreated at a lower temperature than in Example 4. At  $T=300^{\circ}\text{C}$ ,  $P=30$  Bar inlet hydrogen partial pressure (without taken into account the evaporated diesel) and  $\text{LHSV}=4\text{h}^{-1}$  the PAH are removed down to XX wt% di-aromatics and YY wt% tri-aromatics. The specific gravity (SG 60/60) is 0.8496. A Ni-Mo on alumina catalyst is used in this test. Again it is clear that a large amount of the poly-aromatic compounds can be removed at lower temperature (and the same pressure) due to the shift in equilibrium. Again there is virtually no further sulphur removal in this low-temperature hydrotreatment.

**Claims**

1.           A process for reducing content of sulphur compounds and polyaromatic hydrocarbons in a hydrocarbon feed  
5   having a boiling range between 120°C and 450°C, which process comprises in combination  
contacting the feed and hydrogen over a hydrotreating catalyst and hydrotreating feed at hydrotreating conditions,  
cooling the hydrotreated effluent and hydrogen-rich gas  
10   from the hydrotreating reactor,  
contacting said effluent and hydrogen gas over a hydrotreating catalyst in a post-treatment reactor at a temperature sufficient to lower the polyaromatic hydrocarbon content.  
15
2.           A process of claim 1, wherein the temperature in the post-treatment reactor is between 50°C and 150°C lower than the outlet temperature of the hydrotreater.
- 20   2.           A process of claim 1, wherein the LHSV in the post treatment reactor is between 2 and 20 times the LHSV in the hydrotreating reactor.
- 25   3.           A process of claim 1, wherein the post-treatment is conducted in a final bed of the hydrotreating reactor.
4.           A process of claim 1, wherein the feedstock is characterised by having a 50% boiling point between 200°C and 350°C.



5. A process of claim 1, wherein the hydrotreating catalyst used in the post-treatment reactor is a composite of Group VI-B and/or Group VIII metal on a porous refractory inorganic oxide.

5

6. A process of claim 5, wherein the metals are nickel and molybdenum, or nickel and tungsten.

7. A process of claim 6, wherein the porous refractory inorganic oxide is alumina or silica-alumina.

10

**ABSTRACT**

A process for reducing content of sulphur compounds and polyaromatic hydrocarbons in a hydrocarbon feed having a boiling range between 120°C and 450°C, which process comprises in combination contacting the feed and hydrogen over a hydrotreating catalyst and hydrotreating feed at hydrotreating conditions, cooling the hydrotreated effluent and hydrogen-rich gas from the hydrotreating reactor, contacting said effluent and hydrogen gas over a hydrotreating catalyst in a post-treatment reactor at a temperature sufficient to lower the polyaromatic hydrocarbon content.